

CLAIMS

1. A heterogeneous procatalyst comprising:
a titanium species,
a hydrocarbon-soluble transition metal compound having a structure $M(OR^1)_z$, where:
 M is a non-reducing transition metal other than titanium, the non-reducing transition metal being in an oxidation state of +2 or +3;
 each R^1 is independently (C_1-C_{30}) hydrocarbyl or $-C(O)R^{11}$, where R^{11} is (C_1-C_{30}) hydrocarbyl; and
 z is 2 or 3;
 wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one $-Si(R^S)_3$, where each R^S is (C_1-C_{30}) hydrocarbyl;
a chlorinating agent having a structure $A(Cl)_x(R^2)_{3-x}$, where:
 A is aluminum or boron;
 R^2 is (C_1-C_{30}) hydrocarbyl; and
 x is 1, 2, or 3; and
a magnesium chloride component.
2. The procatalyst according to claim 1, wherein M is chosen from zinc, copper, cobalt, manganese, iron, or chromium.
3. The procatalyst according to claims 1 to 2, wherein $M(OR^1)_z$ is aliphatic or cycloaliphatic hydrocarbon-soluble.
4. The procatalyst according to claims 1 or 2, wherein the procatalyst further comprises a vanadium component.
5. The procatalyst according to claim 4, wherein the vanadium component is chosen from VX_4 , VOX_3 , or $VO(OR^3)_3$, where each X is independently a halogen atom or; and R^3 is (C_1-C_{20}) hydrocarbyl or $-C(O)R^{31}$, where R^{31} is (C_1-C_{30}) hydrocarbyl, wherein each R^3 and R^{31} may optionally be substituted with one or more halogen atoms or one or more $-Si(R^S)_3$ where each R^S is independently (C_1-C_{30}) hydrocarbyl.

6. The procatalyst according to any one of the preceding claims, wherein the ratio of transition metal to titanium is from 0.1 to 10 (mole/mole).
7. The procatalyst according to claim 5 or claim 6, wherein the ratio of vanadium to titanium is from 0.1 to 10 (mole/mole).
8. The procatalyst according to any one of the preceding claims, wherein the ratio of magnesium chloride to titanium is from 1 to 100 (mole/mole).
9. The procatalyst according to any one of the preceding claims, wherein the magnesium chloride component has a surface area of greater than or equal to 100 m²/g as measured according to the BET method.
10. A process for polymerizing ethylene-based polymers, the process comprising:
 - contacting ethylene and optionally one or more α -olefins in the presence of a catalyst system, wherein the catalyst system comprises a heterogeneous procatalyst, the heterogeneous procatalyst comprising:
 - a titanium species,
 - a hydrocarbon-soluble transition metal compound having a structure $M(OR^1)_z$, where:
 - M is a transition metal in an oxidation state of +2 or +3; and
 - each R^1 is independently (C_1-C_{30}) hydrocarbyl or $-C(O)R^{11}$, wherein R^{11} is (C_1-C_{30}) hydrocarbyl; and
 - z is 2 or 3;
 - wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one $-Si(R^S)_3$, where each R^S is (C_1-C_{30}) hydrocarbyl;;
 - a chlorinating agent having a structure $A(Cl)_x(R^2)_{3-x}$, where:
 - A is aluminum or boron;
 - R^2 is (C_1-C_{30}) hydrocarbyl; and
 - x is 1, 2, or 3; and
 - a magnesium chloride component.
11. The process according to claim 10, wherein M is chosen from zinc, copper, cobalt, manganese, iron, or chromium.

12. The process according to claim 10 or claim 11, wherein transition metal compound is non-reducing.
13. The process according to any one of claims 10 to 12 wherein the heterogeneous procatalyst further comprises a vanadium component.
14. The process according to claim 13, wherein the vanadium component is chosen from VX_4 , VOX_3 , or $VO(OR^3)_3$, where each X is independently a halogen atom or (; and R^3 is (C_1-C_{20}) hydrocarbyl or $-C(O)R^{31}$, where R^{31} is (C_1-C_{30}) hydrocarbyl, wherein each R^3 and R^{31} may optionally be substituted with one or more halogen atoms or one or more $-Si(R^S)_3$ where each R^S is independently (C_1-C_{30}) hydrocarbyl.
15. The process according to any one of claims 10 – 14, wherein the ratio of transition metal to titanium is from 0.1 to 10 (mole/mole).
16. The process according to claim 12 or claim 13, wherein the ratio of vanadium to titanium is from 0.1 to 10 (mole/mole).
17. The process according to any one of claims 10 – 16, wherein the ratio of magnesium chloride to titanium is from 5 to 100 (mole/mole).
18. The process according to any one of claims 10 – 17, wherein magnesium chloride support has a surface area of greater than or equal to $100\text{ m}^2/\text{g}$ as measured with the BET method.
19. The process according to any one of claims 10 – 18, wherein the catalyst system further comprises an activator.
20. The process according to claim 19, wherein the activator comprises an alkyl aluminum compound.
21. The process according to any one of claims 10 – 20, wherein the polymerization process is a solution polymerization process.
22. A process of making the procatalyst, the process comprising:
preparing a $MgCl_2$ slurry in a hydrocarbon solvent; and
mixing a chlorinating agent, a hydrocarbon-soluble transition metal compound, and a titanium species into the $MgCl_2$ slurry,

wherein

the transition metal compound has a structure $M(OR^1)_z$, where:

M is a non-reducing transition metal in an oxidation state of +2 or +3;

each R^1 is independently (C_1-C_{30}) hydrocarbyl or $-C(O)R^{11}$, wherein R^{11} is (C_1-C_{30}) hydrocarbyl; and

z is 2 or 3;

wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one $-Si(R^S)_3$, where each R^S is (C_1-C_{30}) hydrocarbyl; and

the chlorinating agent has a structure $A(Cl)_x(R^2)_{3-x}$, where:

A is aluminum or boron;

R^2 is (C_1-C_{30}) hydrocarbyl; and

x is 1, 2, or 3.

23. The process of making the procatalyst according to claim 22, wherein the hydrocarbon solvent comprises non-halogenated (C_3-C_{30}) alkyl or non-halogenated (C_3-C_{30}) cycloalkyl.